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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G08B 13/24, H01F 41/24 — A1

(11) International Publication Number: **WO 99/53458**

(43) International Publication Date: 21 October 1999 (21.10.99)

(21) International Application Number: PCT/CA99/00296

(22) International Filing Date: 7 April 1999 (07.04.99)

(30) Priority Data:
2,234,760 15 April 1998 (15.04.98) CA

(71) Applicant *(for all designated States except US)*: MXT INC. [CA/CA]; Suite 104, 1744 William, Montreal, Quebec H3J 1R4 (CA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: RUDKOWSKI, Piotr [CA/CA]; 3 Rue Blue Jay, Dollard des Ormeaux, Quebec H9A 3H4 (CA). STROM–OLSEN, John [CA/CA]; 443 Lansdowne, Westmount, Quebec H3Y 2V2 (CA). LIU, Zhi, Hui [CN/CA]; Apartment 509, 1445 du Fort, Montreal, Quebec H3H 2C3 (CA).

(74) Agents: MURPHY, Kevin, P. et al.; Swabey Ogilvy Renault, Suite 1600, 1981 McGill College Avenue, Montreal, Quebec H3A 2Y3 (CA).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: DEACTIVATABLE MAGNETIC MARKER AND METHOD FOR PRODUCTION THEREOF

(57) Abstract

A deactivatable marker, as used for example for product security identification or authentication, comprises a deactivatable magnetic substrate, typically of a soft magnetic material, an electrolessly deposited, protective layer, and a deactivating layer, typically of semi–hard magnetic material. The deactivating layer may also be applied electrolessly, following deposition of the protective layer, and can be comprised of the same material as the protective layer. Electroless deposition allows the deactivation process to be applied to a multitude of fine fibers, either as an assembly of separate fibers or as an array of fibers supported in a non–conducting web, which can be subsequently used for the manufacture of deactivatable markers in various forms.

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DEACTIVATABLE MAGNETIC MARKER AND METHOD FOR PRODUCTION THEREOF

TECHNICAL FIELD

This invention relates to a deactivatable magnetic marker, a process for producing the deactivatable magnetic marker and use of the deactivatable magnetic marker in an electronic surveillance system.

BACKGROUND ART

Electronic monitoring systems are known which electronically monitor the removal or passage of goods from a protected area, such as a site of purchase of the goods as in a store or a site of use of the goods as in a reference library.

Exit from the protected area involves passage through an interrogation zone which detects the presence of a marker on the goods if the goods are being improperly removed from the protected area.

In a magnetic electronic surveillance system the marker comprises a magnetic material; a continuous alternating magnetic interrogation field is generated in the interrogation zone; when the magnetic material of the marker is exposed to this magnetic interrogation field it is driven into and out of magnetic saturation producing a characteristic detectable disturbance of the interrogation field, which in turn generates an audible or visual alarm signal.

A deactivating element accompanies the marker which is able to deactivate the marker for legitimate or authorized removal of the goods from the protected site, such as when the goods have been purchased in a store housing the protected site. The deactivating element is a magnetizable material which, when magnetized, produces a magnetic field which generates magnetic saturation in the marker to a degree that the magnetic interrogation field does not drive the marker into and out of saturation so that no characteristic detectable disturbance of the interrogation field is developed.

Prior markers are frequently of cumbersome size and are applied to the manufactured product by the distributor or merchant rather than by the manufacturer.

It would be advantageous to provide a deactivatable marker of small size, such as a fiber, which might be incorporated in the product during manufacture.

An improved marker is described in U.S. Patent 5,401,584, Minasy et al, in which semi-hard magnetic material is deposited directly on a soft magnetic strip or ribbon which defines a surveillance marker. The direct deposition is typically an electrodeposition, for example, electroplating, or by vacuum deposition or sputtering.

Electrodeposition requires constant electrical contact of the magnetic strip with electrodes. Vacuum deposition and sputtering require unobstructed access to the strip surface to be coated.

The technique of the afore-mentioned U.S. Patent is not amenable to deposition of semi-hard magnetic material on a soft magnetic fiber (as described, for example, in US patent 5,003,291). Electrodeposition of semi-hard magnetic material directly on a soft magnetic fiber can result in deterioration of the magnetic and mechanical characteristics of the fiber. Electroplating of the hard magnetic material on the soft magnetic fiber can cause partial crystallization on the fiber surface, destroying the magnetic characteristic; electroplating can also cause hydrogen embrittlement in the soft magnetic fiber altering both the physical and the mechanical characteristics. Furthermore the technique of electroplating, requires that the fibers be individually separate and that electrical contact be made to all the fibers to be coated. The requirement to keep the fibers physically separated during the coating process also causes major complications to the vacuum deposition and sputtering processes also proposed in U.S. Patent 5,401,584.

DISCLOSURE OF THE INVENTION

This invention seeks to provide an improved deactivatable marker.

The invention also seeks to provide a method for producing the improved deactivatable marker.

In accordance with one aspect of the invention there is provided a deactivatable magnetic marker comprising: i) a deactivatable magnetic substrate adapted to provide a desired magnetic signal, and ii) a layer deposited on said substrate selected from: a) an electrolessly deposited

deactivating layer, and b) a composite layer comprising an electrolessly deposited intermediate layer on said substrate and a deactivating layer on said intermediate layer, said deactivating layer being of magnetizable material of higher magnetic coercivity than said magnetic substrate such that, as magnetized, said deactivating layer deactivates said magnetic substrate.

In accordance with another aspect of the invention there is provided a process for producing a deactivatable magnetic marker comprising: i) electrolessly depositing on a deactivatable magnetic substrate, a layer selected from: a) a deactivating layer, and b) an intermediate layer, and ii) when said layer is said intermediate layer b), depositing a deactivating layer on said intermediate layer, said magnetic substrate being adapted to provide a desired magnetic signal, and said deactivating layer being of magnetizable material of higher coercivity than said magnetic substrate such that, as magnetized, said deactivating layer deactivates said magnetic substrate.

The electroless deposition may be electroless-plating or immersion plating.

In accordance with still another aspect of the invention there is provided a product label or tag having a marker of the invention incorporated therein.

In accordance with still another aspect of the invention there is provided a packaging for a product having a marker of the invention incorporated therein.

DESCRIPTION OF THE BEST MODES

Deactivatable Marker

The magnetic substrate of the deactivatable marker is more especially of a soft magnetic material, which is more especially in the form of a fiber or a web of fibers. Suitably the fiber or the fibers of the web have a diameter of 5 to 100 μm, more usually 15 to 40 μm. Suitably the fibers are amorphous and are made by a melt extraction process.

Soft magnetic materials are characterized by high permeability and low coercivity. Typical soft magnetic materials are permalloys, amorphous nickel-iron alloys and amorphous iron-cobalt alloys.

Soft magnetic material employed in the marker of the invention suitably has a coercivity below 1 Oe and in particular will have a magnetic remanence near zero, and typically within 1% of the saturated magnetization.

An electrolessly deposited layer is formed on the magnetic substrate either as the deactivating layer itself or as an intermediate or buffer layer between the magnetic substrate and a subsequently deposited deactivating layer of magnetizable material.

Thus in one embodiment of the invention the deactivating layer is electrolessly deposited directly on the magnetic substrate. In another embodiment an intermediate or buffer layer is deposited on the magnetic substrate and the deactivating layer is deposited on the intermediate or buffer layer. In this latter embodiment the deactivating layer may be deposited electrolessly or by other techniques such as electrodeposition, for example, by electroplating or sputtering. The intermediate or buffer layer serves a protective function, preventing and reducing deterioration of the physical or magnetic characteristics of the magnetic substrate, which deterioration is experienced when the deactivating layer is deposited directly on the magnetic substrate by electrodeposition.

The electrolessly-deposited intermediate or buffer layer may be a non-magnetic or a soft magnetic layer. Particularly suitable non-magnetic or soft magnetic layers are Ni-P alloys and Cu-P alloys. It has also been found that the interfaces produced by the electroless activation process, typically applied to substrates so as to render them autocatalytic and thereby suitable for subsequent electroless deposition, do not interfere with the magnetic deactivation process. Such active surfaces can result, for example, from the treatment of the substrate with stannous and palladium containing solutions. In addition to stannous and palladium activation, it should be understood that any material that can be deposited on the surface in atomic or very small quantities so as to render the surface autocatalytic can be employed to achieve the same result.

Electroless deposition in the present invention contemplates electroless plating or immersion plating. Electroless plating is the controlled autocatalytic deposition of a continuous film or coating by

chemical interaction, typically in a solution of a metal salt and a chemical reducing agent. In electroless deposition the electrons for reduction are supplied by the chemical reducing agent.

Unlike conventional electroplating, no electrical current is required for deposition, and the electroless-plating bath provides a deposit that follows the contours of the substrate exactly, without build-up at edges and corners.

Electroless plating employs a solution which contains the ions of the metal to be plated together with a reducing agent which, in the presence of a suitable catalyst, reduces the ions to metal. The catalyst is typically a metal surface, which may be of the same metal as that to be plated. Generally cobalt alloys are themselves catalytic and do not require a catalytic layer. In the case of amorphous fibers, however, an additional layer or surface treatment is required to prevent degradation and to render the surface suitably catalytic.

In electroless plating, metal ions are reduced to metal by the action of chemical reducing agents, which are simply electron donors. The metal ions are electron acceptors, which react with electron donors. The catalyst is the workpiece or metallic surface, which accelerates the electroless chemical reaction allowing oxidation of the reducing agent.

Immersion plating takes place when the surface to be plated is partially dissolved by the plating bath; for instance, when metal A is immersed in a solution containing ions of metal B, under certain conditions a small quantity of metal A is dissolved from the surface and replaced by an electrochemically equivalent quantity of metal B.

Immersion baths can only be used for specific combinations of base and plated metals, while true electroless baths for electroless-plating work on any catalytic surface, except on certain metals which inhibit the reaction. Furthermore, immersion plating produces only a thin coating usually about 1 to 2 microns, since the displacement reaction is gradually inhibited by deposited metal. True electroless baths may deposit much heavier coatings virtually unlimited in thickness, since the reducing agent is contained in the solution.

Suitably the intermediate layer, applied as a separate electroless layer, has a thickness of 0.2 to 10 μm, more usually 0.5 to 6 μm.

If, however, the electroless process forms the deactivation layer then its thickness has to be such as to suitably perform the required deactivation process

The magnetic substrate in the form of a fiber or a web of fibers may be incorporated in a plastic support, for example, a sheet or strip of a non-woven plastic material such as polyester. The fiber or web is incorporated in the support so as to be partially or totally exposed at a surface of the support (and within the support should the support be porous), an activating layer for the electroless deposition and the subsequent electrolessly deposited layer are disposed on the exposed portions of the fiber or web and support. In this case the procedure may involve incorporation in the plastic support, sensitizing the plastic and electroless deposition of the intermediate layer followed by deposition of the deactivating layer.

It has also been found to be possible to selectively activate and electrolessly coat the magnetic fibers in such a non-woven plastic support, such that the deposition of the deactivation layer occurs preferentially on the fiber and not on the support material. This selective deposition is important in that it reduces the consumption of deactivating materials, which tend to be expensive.

In a further embodiment certain areas of the fiber or web may also be covered by an inert coating layer so as to prevent deposition of the intermediate and/or deactivation layers in these areas. In this way the fiber or web will be only partly covered with the deactivating layer, so that the deactivating layer is deposited in a non-continuous layer, in a desired pattern. This will allow for magnetic flux pinning. This procedure is easily applied when the fibers are contained in a sheet or thread like support, which can be selectively covered with liquid monomers or plastics, which are subsequently cured, or with lacquers, varnishes or resists that restrict the access of the electroless plating solutions to the selected portions of the fibers in the support.

Suitable deactivating layers are based on Co, Fe or Ni alloys, for example, semi-hard Co-P alloys, semi-hard Fe-P alloys and semi-hard alloys containing at least 99%, by weight Ni.

The magnetizable material, as magnetized, forms a semi-hard magnet having coercivity between 10 Oe and 300 Oe, preferably between 30 Oe and 150 Oe.

The deactivating layer suitably has a thickness of 5 to 35 μm.

The deactivatable marker fibers may be employed directly as markers by direct incorporation in a product such as a garment, or they may be incorporated in a body member of a product label or tag which is to be attached to the product. Suitably the body member may be of paper, plastic or textile material.

The deactivatable marker fibers may also be formed directly in a body member. Thus the soft magnetic fibers may be incorporated in a dielectric substrate, for example, a plastic substrate, such that the dielectric substrate provides the protective coating. Likewise the marker fibers may be incorporated in packaging for a product.

The use of electroless deposition to form the deactivation layer or the intermediate layer is not obvious, as electroless deposition is characterized by complete coverage of the surface on which the deposition takes place. Complete coverage of the soft magnetic element, as exemplified by a fiber of defined length, would imply that the demagnetizing field, generated upon magnetization of the magnetically semi-hard deactivation layer, would not penetrate the inner soft magnetic material of the magnetic substrate, and thus not cause the desired magnetic saturation. The fact that such layers do indeed show the desired deactivation effect, is not fully understood, but could be due to the lack of uniformity of the deposit, particularly when relatively thick layers are electrolessly deposited. Non-uniform layers would demonstrate the desired deactivation effect as taught by Petersen in US Patent 3,747,086. This magnetic non-uniformity could be caused by the physical form of the deposit, local compositional changes or a combination of both of these factors.

EXAMPLES

A) Formation of the activation and intermediate layers and the deactivating layer

Example 1

This illustrates the production of the intermediate or protective layer employing an electroless bath:

a) Electroless copper plating

As cast 5 grams of melt extracted fibers were degreased in 99% pure alcohol and rinsed, the fibers were sensitized for 120 seconds in an acidic solution containing stannous ions:

Stannous chloride, dihydrate	30 g/l
Hydrochloric acid (37%)	75 ml/l
Non-ionic wetting agent	7 drops

The fibers were rinsed with deionised water, and activated by immersing in an acidic solution containing ions of palladium for about two minutes:

Palladium chloride	0.3 g/l
Hydrochloric acid	15 ml/l
Non-ionic wetting agent	7 drops

The activated fibers were rinsed with deionised water and introduced into an electroless copper plating bath to form the intermediate layer:

Copper sulphate, pentahydrate	10 g/l
Sodium potassium tartate	45 g/l
Formaldehyde (37%)	15 ml/l
Sodium hydroxide	15 ml/l
Sodium carbonate	5 g/l
Potassium cyanide	1-10 ppm
Wetting agent	0.5 ml/l

The bath was operated at 25°C; at pH 12 controlled by addition of sodium hydroxide for a time of about 15 minutes, the resulting fibers were rinsed with deionised water and dried.

b) Electroless nickel plating

As cast 5 grams of melt extracted fibers were degreased in 99% pure alcohol and rinsed, the fibers were activated by immersing in an acidic solution:

Chromic acid	10 g/l
Sulfuric acid	5 g/l

The fibers were rinsed with deionised water and introduced into an electroless nickel plating solution to form the intermediate layer:

Nickel chloride	45 g/l
Sodium hypophosphite	11 g/l
Sodium citrate	100 g/l
Ammonium chloride	50 g/l

The bath was operated at pH 8.5 to 9.0 and a temperature of 90 to 100°C for a time of 30 minutes (the bath had a plating rate of 7.5 micrometers per hour); the resulting fibers were rinsed with deionised water and dried.

Example 2

The following Example illustrates electro-plating of semi-hard magnetic material on melt extracted fibers, which have been previously coated with an electroless nickel or copper intermediate layer.

5 grams of melt extracted fibers covered with electroless nickel as per Example 1b) were degreased in 99% pure alcohol and rinsed with deionised water; the fibers were connected with a negative electrode and electroplated with semi-hard iron-chromium, using the following bath:

Ferrous sulfate 240 g/l (iron content 48 g/l)

Sulfuric acid to pH 2.8-3.5

Trivalent chromium 5 g/l - 3-5 drops

Plating was performed at room temperature (25°C), and a current was passed through the fibers for an amount of time sufficient to coat the fibers with a layer of 20 microns of iron. The electroplated fibers were rinsed in 99% pure alcohol and dried.

A similar plating operation was performed on fibers that had not been protected with an electroless copper or nickel layer.

Similarly fibers both having and not having a protective electroless copper or nickel layer were plated with a semi-hard nickel-cobalt layer, using the following procedure:

Electroless plated nickel or copper fibers produced as in Example 1 were degreased in 99% pure alcohol and dried. The fibers were connected with a negative electrode and electroplated with a semi-hard nickel-cobalt layer using the following bath and conditions:

Nickel chloride	110 g/l
Cobalt chloride	50 g/l
Ammonium chloride	25 g/l
Sodium sulphate	50 g/l
Sodium phosphite	3 g/l

at room temperature (25°C). A current was passed through the fibers for an amount of time sufficient to coat the mass of fibers with a layer of 20 microns of cobalt. The electroplated fibers were rinsed in 99% pure alcohol and dried.

Example 3

Electroless deposition of cobalt alloys as the semi-hard magnetic deactivation layer.

As cast 5 grams of melt extracted fibers were degreased in 99% pure alcohol and rinsed, the fibers were sensitized by immersion for 120 seconds in an acidic solution containing stannous ions:

Stannous chloride, dihydrate	30 g/l
Hydrochloric acid (37%)	75 ml/l
Non-ionic wetting agent	7 drops

The fibers were rinsed with deionised water, and activated by immersing in an acidic solution containing ions of palladium:

Palladium chloride	0.3 g/l
Hydrochloric acid	15 ml/l
Non-ionic wetting agent	7 drops

The activated fibers were then thoroughly rinsed in deionized water and then immersed in a electroless cobalt alloy plating solution:

Cobalt sulfate	25 g/l
Ferrous sulfate	1.5g/l
Nickel sulfate	0.7g/l
Manganese sulfate	0.8g/l
Sodium hypophosphite	20 g/l
Sodium citrate	50 g/l
Ammonium sulfate	50 g/l

The solution was maintained at a pH of 8.5, by additions of ammonium hydroxide, and at a temperature of 90°C, and plating was continued for three hours to provide an alloy coating of approximately 20 microns on the fibers. The resulting fibers were rinsed with deionised water and dried.

Example 4.

Activation of cobalt alloy soft magnetic fibers for electroless deposition and application of an electroless cobalt alloy-deactivating layer.

As cast 5 grams of melt extracted fibers were degreased in 99% pure alcohol and rinsed, the fibers were made electro-catalytically active, as taught in US patent 5,431,959, by immersion in a solution comprising:

Ammonium sulfate	25g/l
Sulfuric acid	25g/l

for a period of half an hour at room temperature.

The activated fibers were then thoroughly rinsed in deionized water and then immersed in an electroless cobalt alloy plating solution:

Cobalt sulfate	25 g/l
Ferrous sulfate	1.5g/l
Nickel sulfate	0.7g/l
Manganese sulfate	0.8g/l
Sodium hypophosphite	20 g/l
Sodium citrate	50 g/l
Ammonium sulfate	50 g/l

The solution was maintained at a pH of 8.5, by additions of ammonium hydroxide, and at a temperature of 90°C, and plating was continued for three hours to provide an alloy coating of approximately 20 microns on the fibers. The resulting fibers were rinsed with deionised water and dried.

Example 5.

Selective activation and coating of soft magnetic fibers contained in a non-woven polymeric sheet

A sample of porous, non-woven polyester sheet having a thickness of approximately 125 microns and containing 5 grams of melt extracted fiber per square meter of area was degreased in 99% pure alcohol and rinsed. The contained, melt extracted fibers were sensitized by immersion in an acidic solution containing stannous ions for 120 seconds:

Stannous chloride, dihydrate	30 g/l
Hydrochloric acid (37%)	75 ml/l
Non-ionic wetting agent	7 drops

The sample was rinsed with deionised water, and activated by immersing in an acidic solution containing ions of palladium:

Palladium chloride	0.3 g/l
Hydrochloric acid	15 ml/l
Non-ionic wetting agent	7 drops

The sample containing the activated fibers was then carefully rinsed in deionized water and coated with an electroless cobalt alloy as in Example 4.

The resulting sheet containing the coated fibers was then rinsed with deionised water and dried.

Examination of the sheet showed that the electroless deposit was largely confined to the melt extracted fibers contained in the porous sheet.

Example 6.

Activation of melt extracted soft magnetic fibers contained in a non-woven, polymeric sheet.

A sample of porous, non-woven polyester sheet having a thickness of approximately 125 microns and containing 5 grams of melt extracted fiber per square meter of area was degreased in 99% pure alcohol and rinsed. The fibers, contained therein, were made electro-catalytically active by immersion in a solution comprising:

Ammonium sulfate	25g/l
Sulfuric acid	25g/l

for a period of half an hour at room temperature

The sample containing the activated fibers was then thoroughly rinsed in deionized water and then thoroughly rinsed in deionized water and coated with an electroless cobalt alloy as in Example 4.

The resulting sheet containing the coated fibers was then rinsed with deionised water and dried.

Examination of the sheet showed that the electroless deposit was largely confined to the melt extracted fibers contained in the porous sheet.

All solutions were prepared by dissolving reagent grade chemicals in distilled water and were used without further treatment or purification.

B) Magnetic properties and deactivation results

Following the procedure of Example 2, magnetic fibers of a soft magnetic material were coated electrolessly with an intermediate or buffer layer of Ni-P, in a thickness of 3 μm. These fibers were electroplated so as to form an appropriate thickness of a semi-hard magnet material of Fe-Cr alloy, so as to render the fibers suitably deactivatable. Uncoated soft magnetic fibers were also electroplated under the same conditions with the semi-hard magnet material of Fe-Cr alloy. In this way there were produced

samples of deactivatable markers with and without the intermediate protective layer of the invention.

Induced magnetic signals from both samples were compared. Signals from the non-protected fibers exhibited a deterioration of up to 90%, whereas the signal from the protected fibers changed by less than 5%. The observed reductions in signal for the protected fibers were determined to be in accordance with the expected signal reductions associated with the eddy currents induced in the protective intermediate layer and in the semi-hard demagnetizing layers, whereas the loss in signal for the unprotected fibers showed a much larger effect.

Similar results were obtained with intermediate protective layers based on electrolessly deposited Cu and with deactivation layers comprising nickel-cobalt alloys.

Samples with the protective coatings produced reliable deactivatable tags with strong, stable signals, and the signals were not affected by mechanical stress.

Fibers coated as per Example 3 had the following properties:

Sample Number	Coating Thickness microns	Magnetic properties				Deactivation Efficiency	
		H_c (Oe)	M_s (emu/g)	M_r (emu/g)	Squareness ratio	Signal Drop	Stan. Dev.
1	23.5	45	101.3	24.7	0.24	83%	15%
2	22.2	35	114.9	41.4	0.36	94%	7%
3	20.3	21	123.9	56.9	0.46	94%	6%
4	18.9	32	113.7	53.5	0.47	93%	10%
5	18.2	23	123.4	50.6	0.41	84%	13%

N.B. All samples were plated at a temperature of 88C and at a pH varying between 8.6 and 9.0

Sample markers made from these fibers were readily detected in commercial anti-theft gates, (operating on the electro-magnetic principle), before being subjected to a deactivating field, and the same

markers could not been detected after they had be subjected to a suitable, demagnetizing field.

Fibers coated as per Example 4 had the following properties:

Sample Number	Coating Thickness microns	Magnetic properties				Deactivation Efficiency	
		H_c (Oe)	M_s (emu/g)	M_r (emu/g)	Squareness ratio	Signal Drop	Stan. Dev.
44	22.6	43	106.9	46.0	0.43	94%	2%
49	22.2	48	107.0	46.0	0.43	97%	1%
50	21.0	36	117.0	49.3	0.42	80%	9%
51	19.8	50	110.9	47.7	0.43	76%	8%
52	20.2	45	105.9	47.7	0.45	82%	11%

N.B. All samples were plated at a temperature of 82C and at a pH varying between 8.25 and 8.63

Sample markers made from these fibers were readily detected in commercial anti-theft gates, (operating on the electro-magnetic principle), before being subjected to a deactivating field, and the same markers could not be detected after they had be subjected to a suitable, demagnetizing field.

Markers fabricated from a non-woven polymeric sheet treated as described in Examples 5 and 6 were readily detected in commercial anti-theft gates, (operating on the electro-magnetic principle), before being subjected to a deactivating field, and the same markers could not been detected after they had be subjected to a suitable, demagnetizing field.

CLAIMS

1. A deactivatable magnetic marker comprising:

i) a deactivatable magnetic substrate adapted to provide a desired magnetic signal, and

ii) a layer deposited on said substrate selected from:

a) an electrolessly deposited deactivating layer, and

b) a composite layer comprising an electrolessly deposited intermediate layer on said substrate and a deactivating layer on said intermediate layer,

said deactivating layer being of magnetizable material of higher magnetic coercivity than said magnetic substrate such that, as magnetized, said deactivating layer deactivates said magnetic substrate.

2. A marker according to claim 1, wherein said layer ii) is said electrolessly deposited deactivating layer a).

3. A marker according to claim 1, wherein said layer ii) is said composite layer b).

4. A marker according to claim 3, wherein both said intermediate layer and said deactivating layer are formed by electroless deposition.

5. A marker according to claim 2, wherein said layer ii) is deposited by electroless, immersion plating.

6. A marker according to claim 1, 2, 3, 4, or 5, wherein said deactivating layer, as magnetized, is a semi-hard magnetic layer having a coercivity between 10 Oe and 300 Oe.

7. A marker according to claim 6, wherein said coercivity is between 20 Oe and 50 Oe.

8. A marker according to claim 3 or 6, wherein said intermediate layer is deposited by electroless immersion plating.

9. A marker according to any one of claims 1 to 8, wherein said substrate comprises a soft magnetic fiber.

10. A marker according to claim 10, wherein said fiber is a melt extracted fiber.

11. A marker according to any one of claims 1 to 8, wherein said substrate comprises a soft magnetic fiber incorporated in a plastic support material so as to be exposed at the surface of the support material.

12. A marker according to claim 11, wherein said marker comprises a web of fibers and said support material is a non-woven plastic sheet.

13. A marker according to claim 11, wherein said marker comprises a web of fibers and said support material is a non-woven plastic sheet, in which the deactivating layer is preferentially located on the fibers exposed therein.

14. A marker according to claim 12, wherein said fiber comprises a web of fibers and said support material is a non-woven plastic sheet, in which the deactivating layer is present in a specific pattern on said support and on the web of fibers.

15. A product label or tag having incorporated therein a marker as defined in any one of claims 1 to 14.

16. A product label or tag according to claim 15, comprising a body member or paper, plastic or textile material, said marker being incorporated in said body member.

17. A packaging for a product having incorporated therein a marker as defined in any one of claims 1 to 14.

18. A process for producing a deactivatable magnetic marker comprising:

i) electrolessly depositing on a deactivatable magnetic substrate, a layer selected from:

a) a deactivating layer, and

b) an intermediate layer, and

ii) when said layer is said intermediate layer b), depositing a deactivating layer on said intermediate layer,

said magnetic substrate being adapted to provide a desired magnetic signal, and

said deactivating layer being of magnetizable material of higher coercivity than said magnetic substrate such that, as magnetized, said deactivating layer deactivates said magnetic substrate.

19. A process according to claim 18, wherein said layer deposited in step i) is said deactivating layer a).

20. A process according to claim 18, wherein said layer deposited in step i) is said intermediate layer b).

21. A process according to claim 18, 19 or 20, wherein said deactivating layer, as magnetized, is a semi-hard magnet.

22. A process according to claim 18, 19, 20 or 21, wherein said substrate comprises a melt extracted fiber.

23. A process according to claim 18, 19, 20 or 21, wherein said substrate comprises a web of melt extracted fibers.

24. A process according to claim 18, 19, 20, 21, 22 or 23, wherein said deactivatable magnetic substrate is incorporated in a plastic support material so as to be exposed at the surface of the support material and said layer in step i) is deposited on the exposed substrate and support.

25. A process according to claim 18, 19, 20, 21, 22 or 23, wherein said deactivatable magnetic substrate is incorporated in a plastic support material so as to be exposed at the surface of the support material, which is subjected to an activation process so as to allow the electroless deposition of

step i) to occur preferentially on the deactivatable magnetic substrate exposed therein.

26. A process according to claim 18, 19, 20, 21, 22 or 23, wherein said deactivatable magnetic substrate is incorporated in a plastic support material so as to be exposed at the surface of the support material and said support material is treated with an inert filler material so as to allow the electroless deposition of step i) in a specific pattern on the said support and on the deactivatable magnetic substrate.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 99/00296

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G08B13/24 H01F41/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G08B H01F G09F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 643 376 A (KNOGO CORP) 15 March 1995 (1995-03-15) cited in the application abstract ---	1-26
A	US 3 895 124 A (LOUCH ROBERT WILLIAM) 15 July 1975 (1975-07-15) abstract ---	1-8, 18-21
A	US 5 003 291 A (STROM-OLSEN JOHN O ET AL) 26 March 1991 (1991-03-26) abstract ---	9,10,22
A	US 5 121 106 A (KATARIA VIBHA R ET AL) 9 June 1992 (1992-06-09) abstract --- -/--	12,23

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
13 July 1999	19/07/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Sgura, S

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 99/00296

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 820 938 A (KNAUF SNC) 28 January 1998 (1998-01-28) abstract	16
A	US 4 224 381 A (PATEL PRAVIN K ET AL) 23 September 1980 (1980-09-23) abstract	1-8, 18-21
A	US 5 006 367 A (LANCSEK THOMAS S) 9 April 1991 (1991-04-09) column 2, line 66 - column 3, line 3	1-8, 18-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CA 99/00296

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0643376 A	15-03-1995	US 5401584 A	28-03-1995
		AU 665720 B	11-01-1996
		AU 7140894 A	23-03-1995
		BR 9403475 A	16-05-1995
		CA 2131127 A	11-03-1995
		CN 1106947 A	16-08-1995
		JP 2831575 B	02-12-1998
		JP 7175979 A	14-07-1995
US 3895124 A	15-07-1975	GB 1407677 A	24-09-1975
		AU 463714 B	07-08-1975
		AU 5015172 A	20-06-1974
		BE 793263 A	22-06-1973
		CA 983791 A	17-02-1976
		DE 2262406 A	12-07-1973
		FR 2164726 A	03-08-1973
		IT 972880 B	31-05-1974
		JP 48078037 A	19-10-1973
		LU 66724 A	27-12-1973
		NL 7217441 A	26-06-1973
US 5003291 A	26-03-1991	AT 294389 A,B	15-02-1994
		AU 628900 B	24-09-1992
		AU 4704789 A	05-07-1990
		CA 2006223 A,C	27-06-1990
		CH 682521 A	30-09-1993
		DE 3942722 A	05-07-1990
		DK 662689 A	28-06-1990
		FR 2641104 A	29-06-1990
		GB 2228742 A,B	05-09-1990
		IT 1237587 B	08-06-1993
		JP 2224854 A	06-09-1990
		JP 2752752 B	18-05-1998
		NL 8903139 A	16-07-1990
		SE 504685 C	07-04-1997
		SE 8904347 A	28-06-1990
US 5121106 A	09-06-1992	CA 2057427 A	01-07-1992
EP 0820938 A	28-01-1998	FR 2751614 A	30-01-1998
US 4224381 A	23-09-1980	NONE	
US 5006367 A	09-04-1991	NONE	